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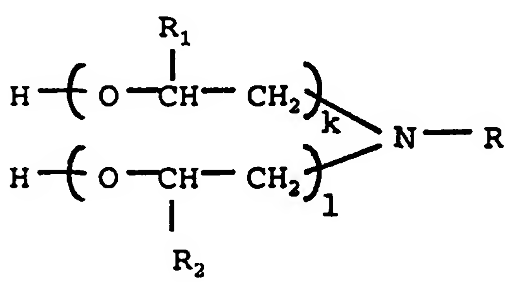

(I)

(57) Abstract

A shale–stabilizing additive is described based on a molecular structure having general formula (I) comprising a polyol containing at least one nitrogen atom, preferably derived from a diamine. The additive can be used for water–based drilling fluid (WBM) to facilitate the drilling process through shales, particularly in environmentally sensitive areas.

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Shale-Stabilizing Additives

This invention concerns drilling fluids, particularly water-based drilling fluids. More specifically, it pertains to additives for drilling fluids. Even more specifically, the invention relates to additives used to prevent shales from adversely affecting drilling operations.

BACKGROUND OF THE INVENTION

Drilling fluids are used in well drilling operations, e.g., during drilling of oil and gas wells. During drilling, drilling fluid is pumped down a drillstring, discharged through ports in the drill bit and returned to the surface via the annulus between the drillpipe and the surrounding formation. The drilling fluid performs a variety of functions including cooling and lubricating the drill bit and drillstring, removing rock cuttings generated during the drilling process and carrying them to the surface, suspending cuttings in the annulus when pumping stops, preventing squeezing in or caving of the formation and keeping formation fluids at bay.

Drilling fluids generally comprise a carrier, a weighting agent and chemical additives. Drilling fluids fall into two main categories: water-based drilling fluids, also known as water based muds (WBM), in which the carrier is an aqueous medium; and oil-based drilling fluids, also known as oil-based muds (OBM), in which the carrier is oil. OBM are technically superior to WBM in certain important respects, including the comparative lack of adverse reactivity of OBM with shales, one of the most commonly encountered rock types during drilling for oil and gas. Use of OBM, however, has the disadvantage of resulting in production of large quantities of oil-contaminated waste products such as cuttings that are difficult to dispose of in an environmentally acceptable way. While use of WBM is environmentally more acceptable than OBM, the performance of WBM, particularly when drilling through water sensitive rocks such as shales, is technically inferior to that of OBM. Shales exhibit great

affinity for water, and adsorption of water by shales causes the shale to swell and produces chemical changes in the rock which produce stresses that weaken the formation, possibly leading to erosion of the borehole or loss of structure. This can lead to drilling problems such as stuck pipe. In addition inferior wellbore quality may hinder logging and completion operations.

Much effort has been put into improving the performance of WBM relative to shales, namely improving the level of so called shale inhibition of WBM. Various chemical additives have been incorporated in WBM in attempts to improve shale inhibition. In particular water soluble glycols, polyhydric alcohols (i.e. chemicals containing more than one hydroxyl group) or polyglycols (i.e. chemicals made using alkylene oxides such as ethylene oxide or propylene oxide) are widely used for this purpose, typically being added to WBM in amounts in the range 3 to 10% by weight. These chemicals can be collectively referred to as Polyols. Polyols used in this way include, for example, glycerols, polyglycerols, glycols, polyalkylene glycols (PAG), eg polyethylene glycols (PEG), polypropylene glycols (PPG) and copolymers of ethylene and propylene glycols, alcohol ethoxylates (AET) and glycol ethers. A typical inhibitive AET is an n-butanol derivative of ethylene oxide. The PAGs can have a range of ethylene oxide: propylene oxide (EO:PO) ratios and can be random or block copolymers; a frequently used material of this type is understood to be a random copolymer with an EO:PO ratio of about 1:1.

Variants of polyalkylene glycols and alcohol alkoxylates are for example described in the International Patent Applications WO-96/24645 and WO-96/24646. Others are found in the European Patent Application EP-A-0495579, the United States Patents US-A-4830765 and US-A-4172800.

The use of amine derivatives in drilling fluids for the prevention of shale swelling is known for example from the European Patent Application EP-A-0702073. In the examples of this patent application, diethylaminoethyl chloride and 2,3

epoxypropyl-trimethylammonium chloride are reacted with glycose or methyl-glycopyranoside to provide a shale stabilizer.

The use of reaction products of trihydroxy alkyl amine with an alkyl halide leading to quaternary alkyl amines as additive for shale swelling inhibitors are described in the United States Patent 5,350,740.

In the United States Patent 3,979,305, polyoxyethylene tertiary fatty amines and condensates, thereof, are described for use in a fluid loss additive composition.

In the United States Patent 4,230,586 an aqueous well-drilling fluid is described comprising at least one non-Newtonian colloidal disperse system , a clay/water slurry, and an emulsifier effective for emulsifying the disperse system in the clay/water slurry. Among the emulsifiers described as being useful are ethoxylated amines and diamine wherein the amine or diamine has at least 12 carbon atoms.

In the European Patent Application EP-A-0255161, a drilling fluid is described comprising a stable oil in water emulsion consisting of water, oil, and at least one surfactant belonging to the class of alkyl amine ethoxylates wherein the ethoxylates are bond to the nitrogen via an ether (oxygen) bridge. The drilling fluid is described as preventing shale swelling by coating the oil out onto the mineral surfaces.

Furthermore, in the United Kingdom Patent GB 1,363,355, a surfactant is described for use in a biological assay system. The surfactant is obtained when ethylene diamine is reacted sequentially with propylene oxide and ethylene oxide in the presence of a catalyst, the polyoxyproylene chains of the surfactant having an average molecular weight of between about 750 and 6750.

Further sources relating to the background of the invention are, for instance, the Society of Petroleum Engineers Reports SPE

25989 (Reduced Environment Impact and Improved Drilling Performance With Water-Based Muds Containing Glycols) and SPE 28818 (Water Based Glycol Drilling Muds - Shale Inhibition Mechanisms) and also Schlumberger Oilfield Review, April 1994, pages 33 to 43 (Designing and Managing Drilling Fluid) .

SPE 28960 (Mechanism of Shale Inhibition by Polyols in Water Based Drilling Fluids) proposes a credible mechanism that adequately describes how such polyols provide shale inhibition. In summary, this publication teaches that two processes are important:

The polyols interact with potassium ions on the surfaces of the fine-grained clay minerals that are present in reactive shales. These potassium ions are hydrated but their low hydration energy means that water is easily removed from the cation and the polyol forms a stable complex. Water is less easily removed from sodium or calcium ions and the resulting cation/polyol complexes are weaker: the authors believe this explains the higher level of inhibition obtained with polyols in the presence of potassium. All the established inhibitive polyols studied by the authors are said to derive the bulk of their activity by this mechanism. Other weakly hydrated cations (eg ammonium or caesium) behave in the same way as potassium.

A second, but minor, contribution to inhibition is observed with currently available EO:PO polymers. Here, the authors provide evidence of interactions between adjacent polyol molecules adsorbed on the clay surfaces. These interactions are independent of the concentration and composition of the aqueous salt solution and, since they are absent in the PEG and n-butanol ethoxylate molecules, they assume them to be due to the intermolecular interactions between mildly hydrophobic methyl groups in the PO portions of the EO:PO copolymers. This interaction is sufficient to make EO:PO polymers mildly inhibitive to shales in distilled water, where molecules such as PEG and AET rarely show any degree of inhibition.

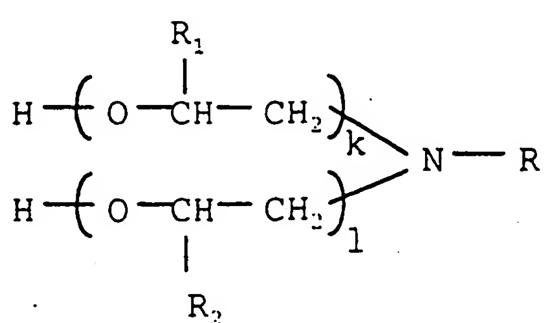
The shale inhibition properties of polyol-containing WBM can be enhanced by incorporation of potassium salts, e.g., potassium chloride, possibly in combination with gypsum. However, the shale inhibition properties of even the best known potassium and polyol-containing WBM are much inferior to those of OBM. Further, the use of potassium can present waste disposal problems, as there are certain regions, e.g., the Gulf of Mexico, where the discharge of potassium to the environment is prohibited or severely restricted. In addition, the use of many types of brine-based WBM can present problems in land drilling where the contamination of ground water by saline drilling waste is considered unacceptable. This waste may contain potassium or other undesirable cations or anions.

Shale swelling is considered as a problem not only in the oil field industry. It is encountered as clay swelling in the mining industry, where this phenomenon causes severe difficulties when dewatering the mineral tailings.

In view of the above, it is an object of the invention to provide a novel polyol compound for inhibiting shale swelling. It is another, more specific object of the invention to provide an additive for WBM.

SUMMARY OF THE INVENTION

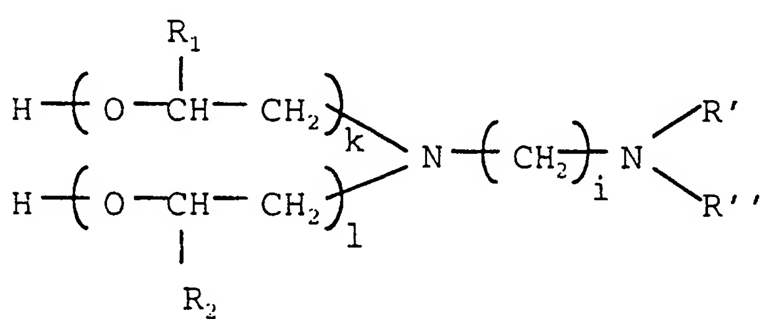
According to a first aspect of the invention, there is a shale-stabilizing additive for water based drilling fluids of the the following general structural formula:



where R_1 and R_2 are H, CH_3, or CH_2-CH_3, depending on the epoxide employed, i.e. EO, PO, or BO, respectively. The sum of k and l is in the range of 2 to preferably 25, with each individual number being equal to or larger than 1. R denotes an arbitrary group, however excluding aliphatic hydrocarbyl residues with 12 carbon atoms or more. Preferably R includes at least one hetero-atom such as nitrogen or oxygen. Hence, the additional group R is not meant to give the novel additive a pronounced amphiphilic characteristic, as its primary use is as a shale swelling inhibitor and not as an emulsifier or a surfactant.

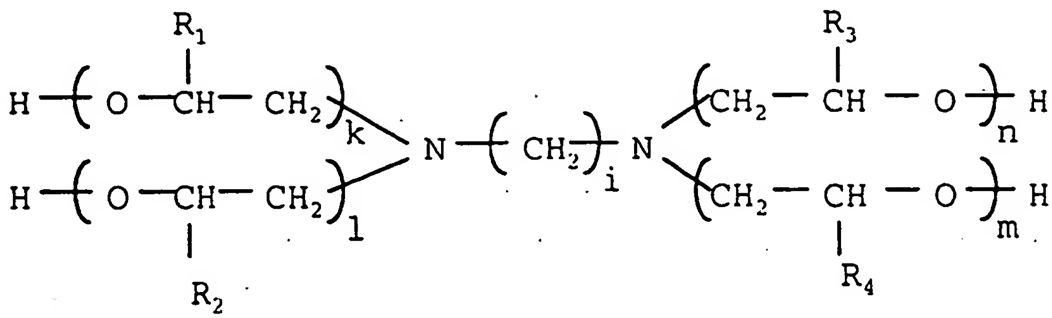
It is further known that surfactants in general raise concerns with respect to their impact on the environmental, particularly the marine environment. It is there more advantageous to avoid selecting as R an aliphatic hydrocarbon residue of 12 or more carbon atoms.

An even more preferred variant of the invention has the general structural formula:



where the length (index: i) of the hydrocarbon chain separating the two nitrogen atoms is preferably in the range of 1 to 10 and R' and R'' are hydrogens or arbitrary groups, however not an aliphatic hydrocarbyl residues with 12 carbon atoms or more. Preferably at R' or R'' include at least one hetero-atom such as oxygen.

An even more preferred variant of the invention has the general structural formula:



where R_1 to R_4 are H, CH_3, or CH_2-CH_3, depending on the epoxide employed, i.e. EO, PO, or BO, respectively. The sum of k, l, m, and n is preferably in the range of 4 to 25, with each individual number being preferably equal to or larger than 1. The length (index: i) of the hydrocarbon chain separating the two nitrogen atoms is preferably in the range of 1 to 10. In case of EDA and HDA, i is 2 and 6, respectively. Such polyols and derivatives thereof are commercially available.

The polyol according to the present invention is preferably used as an additive in water-based drilling fluids (WBM) or in dewatering operations for mineral tailings.

In another aspect, the invention concerns a drilling fluid with 0.1 to 10 weight per cent (wt%) of the novel additives as characterized before. More preferably, the novel additives are used at 1 to 5 wt%.

The additives in accordance with the invention provide higher levels of shale swelling inhibition in the presence of weakly hydrated cations, such as potassium, caesium, and ammonium. Another advantage of the novel additives is the ability to formulate highly inhibitive water based muds without using substantial amount of such salts. In other words, inhibition can be obtained solely from using the additives in freshwater or in combination with salts containing for example sodium, calcium, or magnesium ions, rather than potassium ions. The latter advantage is particularly useful in areas where environmental

concerns prohibit or severely restrict the use of saline drilling fluids.

It is therefore another aspect of the invention to provide an essentially potassium-free WBM. An essentially potassium-free WBM is defined as having less that 3 wt% potassium content, preferably less that 1 wt%, most preferably less than 0.1 w%.

To reduce the impact on the environment, it is desirable to keep the oil content of the initial drilling fluid as low as possible, i.e below 5% or even more preferable below 3%. However, during the drilling of an hydrocarbon bearing formation oil is naturally added to the initial mixture.

It is equally desirable to prepare the initial drilling fluid with a low clay content, i.e below 5% or even more preferable below 3%, as the amount of shale swelling inhibitor which reacts with the initial clay, is no longer available for the treatment of the subterranean formation. Thus, any amount of clay in the initial fluid has to be compensated by an equivalent amount of inhibitor to retain the same level of inhibition downhole.

It can also be expected that the novel additives can improve current methods of dewatering mineral tailings in the mining industry, as today this process is severely hampered by clay swelling.

These and other features of the invention, preferred embodiments and variants thereof, and further advantages of the invention will become appreciated and understood by those skilled in the art from the detailed description following below.

EXAMPLE(S) FOR CARRYING OUT THE INVENTION

The level of shale inhibition provided by different drilling fluid additives and formulations is routinely assessed by a number of laboratory techniques. Tests such as cuttings

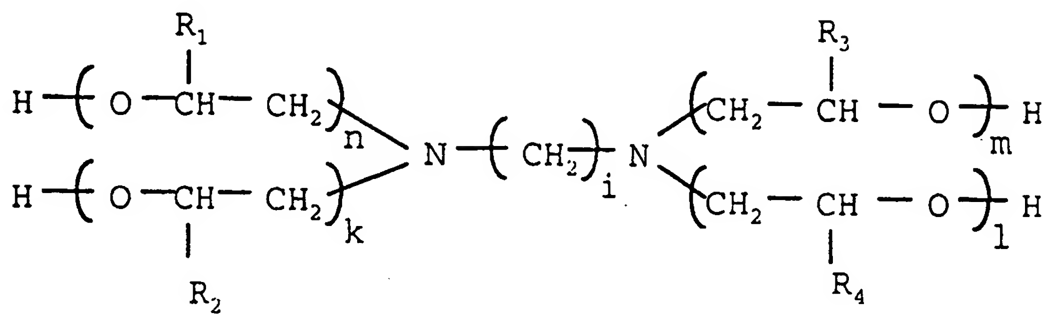
dispersion and shale swelling are suitable for the rapid screening of new additives and are widely use in the industry. A good indication of the inhibitive properties of an additive can also be obtained by a modification of the standard oilfield cuttings dispersion test. This approach is particularly suitable for screening low viscosity, water-soluble species such as polyols and fully formulated drilling fluids containing the additives.

In this test, a known weight of shale cuttings (approximately 20g) is added to a measured volume of test fluid (approximately 350 ml) in a container. The container is rotated such that the cuttings are in a constant state of agitation in the fluid; this encourages breakdown and dispersion of the cuttings if they become softened due to interaction with the test fluid. At the end of the test period, the cuttings that remain undispersed are collected, washed, dried and weighed. The recovered weight is expressed as a percentage of the original weight added to the test fluid. Clearly, the more inhibitive the test fluid, the lower the level of cuttings dispersion and hence the higher the final recovery figure.

The bulk hardness of the shale treated with these polyols can be measured by pushing the shale cuttings soaked in polyol muds through a porous plate. The force (torque) required to extrude the cutting is related to the efficiency of the polyol as a shale stabiliser, i.e., the highest torque values are obtained with the best shale inhibitors.

The examples M1 and M2 in accordance with the inventions are based on a reaction of 1 mole ethylene diamine (EDA) with 5 mole of propylene oxide (M1) or alternatively with 3 moles of propylene oxide and 1 mole ethylene oxide (M2). The examples M3 and M4 are reaction products of 1 mole hexane diamine (HDA) with 4 moles of propylene oxide (M3) or alternatively with 5 moles of mole ethylene oxide (M4).

These examples can be illustrated by the following structural formula:



where R_1 to R_4 are H, CH_3, or CH_2-CH_3, depending on the epoxide employed, i.e. EO, PO, or BO, respectively. The sum of k, l, m, and n is preferably range of 4 to 25, with each individual number being preferably equal to or larger than 1. The length (index: i) of the hydrocarbon chain separating the two nitrogen atoms is preferably in the range of 1 to 10. In case of EDA and HDA, i is 2 and 6, respectively.

Two polyols used for comparison were polyethylene glycol (PEG) and a mixed polyethylene/polypropylene glycol(PAG); both of these are currently used as shale inhibitors in commercial systems. The average molecular weights of these materials are about 600 and 650 respectively. The PAG is a random copolymer of EO and PO with an EO:PO ratio of approximately 1:1.

Table 1 shows the recovery of Oxford shale cuttings from solutions of de-ionised water and 5 wt% active polyol.

TABLE 1

Polyol	Approximate Polyol Composition	Cuttings Recovery (%)
no polyol		3
PEG	Polyethylene glycol	5
PAG	Mixed polyethylene/ polypropylene glycol	16

M1	EDA + 5 PO	78
M2	EDA + 3 PO + 1 EO	83
M3	HDA + 4 PO	48
M4	HDA + 5 EO	51

The results show the improved levels of inhibition provided by fluids which do not contain potassium chloride when EDA or HDA-based polyols are used in place of polyols currently in commercial use.

In the following table bulk hardness data for London Clay cuttings soaked in polyol muds are presented. In some cases the treated shale was to hard to be extruded. In those cases the thickness of the plug remaining in the test apparatus is used to indicate the effectiveness of the additive in question.

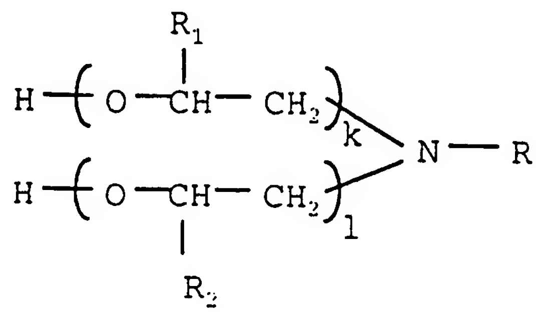
TABLE 2

Polyol	Base	Bulk hardness / Nm	Comments
PEG	water	3.0	All extruded
PAG	water	3.0	All extruded
M1	water	25.3	1mm plug
PEG	potassium chloride	3.0	All extruded
PAG	potassium chloride	5.5	All extruded
M1	potassium chloride	22.5	0.5 mm plug

This second test confirms the effectiveness of amine-based polyol for shale swelling inhibition.

CLAIMS

1. A drilling fluid comprising a shale-stabilizing additive of the following general structural formula:

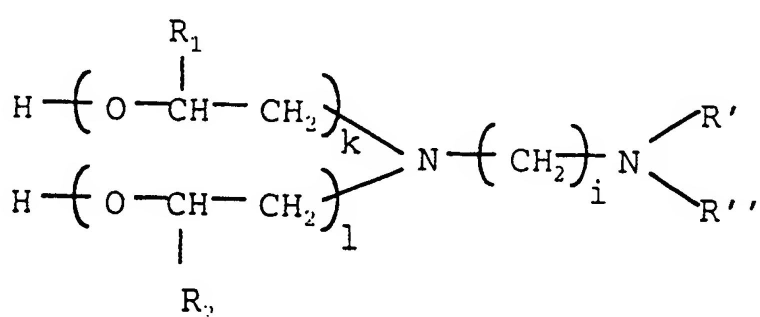


where R_1 and R_2 are H, CH_3, or CH_2-CH_3 and R is an arbitrary group with the exception of an aliphatic hydrocarbon residue with 12 carbon atoms or more.

2. The drilling fluid of claim 1, wherein R includes at least one hetero-atom.

3. The drilling fluid of claim 1 being a water based drilling fluid.

4. The drilling fluid of claim 1, wherein the additive has the general structural formula:

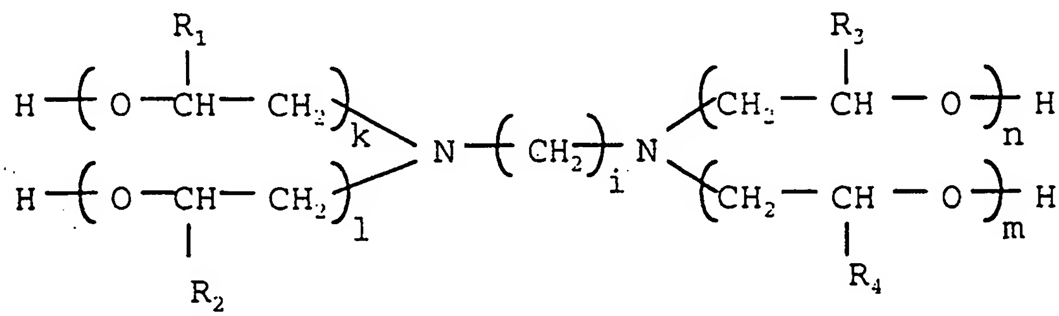


wherein and R' and R'' are hydrogen atoms or arbitrary groups, however excluding an aliphatic hydrocarbon residue with 12 carbon atoms or more.

5. The drilling fluid of claim 4, wherein R' or R'' include at least one hetero-atom.

6. The drilling fluid of claim 4, wherein the length (index: i) of the hydrocarbon chain separating the two nitrogen atoms is in the range 1 to 10.

7. The drilling fluid of claim 1, wherein the additive has the general structural formula:



wherein R_1 to R_4 are H, CH_3, or CH_2-CH_3.

8. The drilling fluid of claim 7, wherein the sum of k, l, m, and n is in the range of 4 to 25, with each individual number being equal to or larger than 1.

9. The drilling fluid of claim 1, comprising 0.1 to 10 weight per cent of the shale swelling additive.

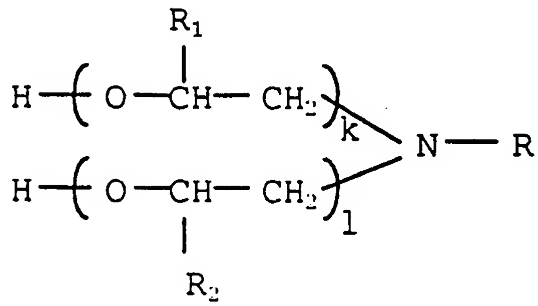
10. The drilling fluid of claim 1, comprising 1 to 5 weight per cent of the shale swelling additive.

11. The drilling fluid of claim 1 having a potassium content of less than 3 weight per cent.

12. The drilling fluid of claim 1, further comprising a viscosifying agent and a fluid loss agent.

13. Method of drilling a well, comprising the steps of

- preparing a water based drilling fluid;
- adding to said water based drilling fluid a shale stabilizing additive of the general formula



;

- pumping said drilling fluid through a drillstring and a drill bit attached to said drillstring; and
- letting said shale stabilizing additive contact formation surrounding said drill bit and/or said drilling string.

INTERNATIONAL SEARCH REPORT

Inte. onal Application No
PCT/GB 98/02377

A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 415 134 A (HALLIBURTON COMP.) 17 August 1979 see page 2, line 10 - page 3, line 5	1,3
X	US 3 123 559 A (P.W.FISCHER) 3 March 1964 see column 2, line 43 - column 3, line 39; claims 1-9	1-12
X	US 3 086 937 A (P.W.FISCHER) 23 April 1963 see column 2, line 60 - column 3, line 27 see claims 1-11; examples 1,3	1-12

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
11 November 1998	18/11/1998

Name and mailing address of the ISA	Authorized officer
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Information on patent family members

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PCT/GB 98/02377

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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